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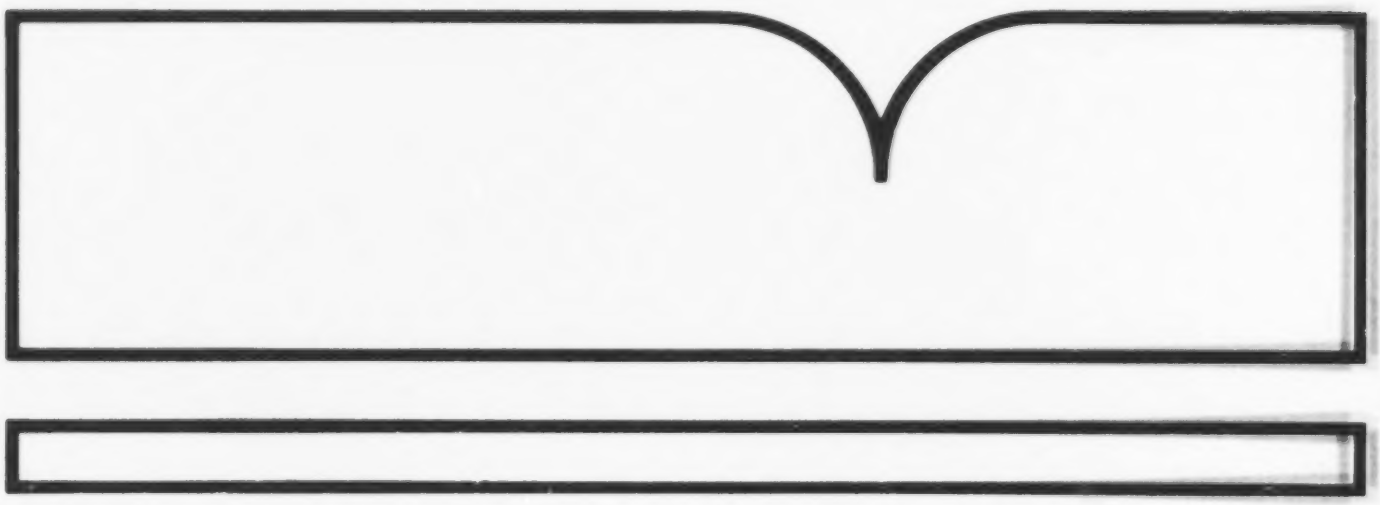

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Direct Calibration of GC/MS Systems Using SRM Gas Cylinders

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ABSTRACT

A cyrogenic trapping system has been developed for use in calibrating GC/MS systems for the analysis of volatile organic compounds. This system provides for direct Standard Reference Material (SRM) traceability on data generated on gaseous samples. The cryogenic trap is a coil of stainless steel tubing immersed in a cryogen to trap and preconcentrate organic species present in a gaseous sample. The trap also contains a heated injection port for the addition of isotopically labeled compounds for use in isotope dilution measurements. The first part of this research is concerned with the development of IDMS as an independent method for the quantification of analytes in gaseous samples to be used as standards. Results are presented for the determination of bromobenzene in nitrogen at nominal concentrations of 1 and 25 ppb. In the second part of the research, a calibration curve method was developed for using these standards in auditing the performance of GC/MS systems. This method is demonstrated on multicomponent aromatic mixtures in the 10 to 200 ppb concentration range. The system using the calibration curve method was evaluated at an independent laboratory and compared with a static dilution bottle calibration curve method.

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Section 1. Introduction

The goal of this project was to develop a system that could be used to introduce organic compounds at low ppb concentrations from a cylinder into a GC/MS system. This system was intended to fill several existing needs. First, it would provide the National Bureau of Standards (NBS) a simplified and improved technique for analyzing the low ppb level organic Standard Refernce Material (SRM) that it was developing through EPA funding for the toxic organic monitoring community. Second, it would provide EPA and other laboratories a means to introduce the gases from cylinders without the need for first collecting them onto an organic substrate. Third, it would provide a means to verify the calibration accuracy of the analytical instruments during performance audits of laboratories.

The first phase of this project involved the design and development of the direct injection system by NBS scientists. The candidate system developed was then evaluated by an independent EPA laboratory during the second phase of the study. The results of the NBS development portion of the project and the EPA evaluation of the system are presented here.

Section 2. Development and Operation of the System

Due to the wide range of concentrations (including the low ppb range) of analytes of interest in ambient air samples and the corresponding standards, direct analysis of the air with methods such as syringe injection or by a fixed volume loop attached to a valve are not always feasible to get the response necessary for quantification. A method is needed to preconcentrate the analytes from the sample to accomodate large sample volumes (up to several liters) in addition to lesser amounts. Some approaches normally used for this involve solid adsorbents such as Tenax in a sorption/desorption process, liquid trapping, or cryogenic trapping and desorption. Most laboratories that deal with environmental air samples use the Tenax method because a sampling device based on a Tenax cartridge can be easily moved about for monitoring air samples in situ and then brought to the laboratory for analysis. However, some problems have been associated with Tenax such as band broadening, background interferences for certain analytes, and incomplete recovery of the analytes from the sorbent. Therefore, an alternate method for introducing a sample, and particularly a calibrant, was desired to avoid any bias that may be present in the Tenax method. Two possibilities considered were liquid trapping (where a measured volume of a gaseous sample is passed through an appropiate solvent in order to trap out the analytes) and the cryogenic trap. The cryogenic trap discussed below was chosen over liquid trapping because it involves fewer steps and, therefore, should be faster and less subject to error.

Cryogenic trapping works by passing the gaseous sample to be analyzed through a cool section of tubing or support material where the organic analytes in the gas will condense on the cold surface. They can then be desorbed and analyzed, usually by a chromatographic method. A diagram of the final version of the cryogenic trap constructed at NBS is shown in Figure 1. The heart of the trap is an approximately 75 cm coil of 0.030 inch (0.076 cm) i.d. stainless steel tubing which has a volume of roughly 0.35 cm^3. The trap includes provision for direct connection to the source of a gas sample and to a heated injection port with a septum for the

injection of liquid samples. The introduction of liquid solutions containing a known amount of the labeled analyte is necessary for the IDMS measurements. The outlet end of the trap is a syringe needle silver-soldered directly to the tubing so that the effluent from the trap can be directly injected into a GC. The coils of the trap are designed to fit into a dewar containing a coolant. Early experiments indicated that nitrogen from the sample cylinder was liquifying in the trap when liquid nitrogen (-196°C) was used as a coolant. A dry ice-ethanol bath was selected as a higher temperature coolant (-72°C) to avoid this problem.

Temperature control of the trap is also important for heating during desorption as well as cooling during trapping since sample desorption is performed by rapidly heating the trap after the coolant was removed. Also, later experiments showed that optimum results were obtained when the trap was slightly warmed while being flushed with sample gas prior to cooling. Therefore, the trap was constructed so that it could be heated by direct resistive heating. The two ends of the trap, from the base of the needle to the beginning of the coil just after the injection port, are electrically connected and heating is accomplished by applying a voltage between the ends and the center tap. Electric current flow is controlled with a variable transformer. Experiments were done to determine the relationship between temperature and the amount of current passed through the trap by monitoring the temperature with a thermocouple as a function of current. In order to warm the trap slightly to 45°C, 6 amps were necessary. For desorption, a temperature of 200°C was obtained with a current of 16 amps. Measurements over different areas of the trap indicated that the heating was sufficiently uniform. The injection port is also resistively heated to approximately 100°C using a separate circuit. The entire assembly is supported on a piece of polytrifluoroethylene.

Figure 2 shows a diagram of the system for trapping and analyzing gaseous samples. The sample cylinder to be analyzed and the helium used for flushing the trap during desorption are connected to the trap via a six port valve used to control switching between the two. The connecting lines used between the sample cylinder, valve, and the trap are the same 0.030 inch (0.076 cm) i.d. stainless steel tubing as for the trap coil. The use of narrow bore tubing minimizes the surface area exposed to the sample and thus reduces the extent of adsorption prior to the trap. In later experiments, a flow controller was installed on the helium line before it entered the valve in order to vary the flow and insure stability of the flow at low desorption flow rates. Desorption flow rates varied from 10-25 mL/min for the IDMS experiments with flow rates as low as 1.5 mL/min for the calibration curve experiments. When trapping a sample, the needle of the trap is first inserted into a septum connected to a wet test flow meter to measure the volume that passes through the trap. The coiled section of the trap is immersed in a coolant for condensing analytes from the gas sample. During desorption of the trapped sample, sample flow is stopped with the six port valve, helium flow through the trap commenced, the needle of the trap inserted into the GC injector, and the coolant removed. Electric current (16 amps) is then applied to the trap for heating.

The GC used in these experiments was equipped with a split/splitless injector and a 30 m DB-5 fused silica capillary column with a film thickness of 1 micron. In later experiments, approximately 1 m of the column was

coiled and immersed in liquid nitrogen during the desorption of the sample to provide on-column focusing of the more volatile components. The Hewlett--Packard 5930 series[1] instrument used is a quadrupole mass spectrometer controlled by a computer with a dual hard disk drive for storage of data. The instrument has been modified so that the column is connected directly to the source of the mass spectrometer through a stainless steel tube. All analyses in this report were made using 70 eV electron impact ionization.

The sample solutions used for response factor determinations and IDMS spiking of the analytes were analyzed on the GC/MS without using the trap. This was done to assess the variance of the instrument and to monitor the stability of the solutions. Response factors are determined by the following formula:

$$RF = \frac{\text{Response labeled analyte}}{\text{Response unlabeled analyte}} \times \frac{\text{Amount unlabeled analyte}}{\text{Amount labeled analyte}}$$

One-to-one solutions of bromobenzene and d5-bromobenzene in n-heptane corresponding to 10 ng, 1 ng, and 0.1 ng on-column amounts were repeatedly injected and the molecular ion and the (M+2) isotope ion were measured for the labeled (m/z 161 and 163) and unlabeled (m/z 156 and 158) analytes in the selected ion monitoring (SIM) mode. Dwell time for each ion was 50 milliseconds. The ratios of the ions 163/158 and 161/156 were compared. Over a 5 day period an average relative standard deviation of less than 6% was obtained for these ratios. These results demonstrated that the GC/MS system was suitably stable to perform IDMS experiments with the necessary sensitivity and precision down to the 1 ppb level.

Injecting solutions through the septum on the cold trap increased the relative standard deviation for the ion ratios of the labeled and unlabeled bromobenzene to 20% over the values measured from direct injection into the GC. These results were considered to be acceptable at the time. The final version of the trap with more uniform coils and an improved injection port gave greatly improved precision as shown in Table 1. No bias was found in the response factors when the trap was used to deliver the solutions instead of direct injection into the GC inlet. Therefore, determination of response factors by direct injection was found to be acceptable.

Section 3. IDMS Quantification of Bromobenzene in Nitrogen

In order to evaluate the performance of the trap using IDMS, measurements were made on well-characterized samples so that the IDMS values could be compared with values obtained by other methods. In this section, the general technique that was developed for these analyses is described. The results using this technique are presented for a preliminary measurement on a 90 ppb cylinder and for several measurements made on 2 SRM cylinders of bromobenzene in nitrogen at the 25 and 1 ppb levels.

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[1] "Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose."

The analysis technique started by making a series of response factor measurements by direct injection of 1:1 response factor solutions of labeled and unlabeled bromobenzene. Response factors were measured again at the end of a series of measurements and the values obtained were averaged. Various methods for flushing the trap and initiating the trapping process were tested in order to optimize the procedure before the analysis of the SRM cylinders. Extensive flushing of the system with the sample prior to trapping and maintenance of the trap at an elevated temperature during flushing was necessary to minimize the effects of adsorption. Flushing the system with even small amounts of helium before trapping gave lower lower for bromobenzene implying that bromobenzene on the surface was removed and left active sites. To circumvent this effect, trapping was initiated by plunging the trap into the dry ice-ethanol bath while the sample flowed through the trap. The internal standard was added by injecting 1.0 uL of a solution of labeled bromobenzene containing approximately the amount of bromobenzene expected to be trapped. Experiments done by adding the labeled compound before and after the trapping showed no bias from this step. The trap needle was then inserted into the GC for the desorption step. The final method for trapping and analyzing the sample is listed in the following procedure:

1. Warm trap to 45°C (6 amps) with He flowing at 25 mL/min.
2. Flush at least 2 L of sample through the warm trap at ~100 mL/min.
3. Raise dewar with dry ice-ethanol over coils of trap to start trapping. Turn off heating current.
4. Stop trapping by switching valve to He flow.
5. Add labeled bromobenzene in hexane through heated injection port.
6. Remove dewar from trap.
7. Immediately insert needle on trap into GC.
8. Desorb at 200°C (16 amps) for 40 seconds.

For the bromobenzene measurements, the column temperature was held at 50°C for 30 seconds and then taken rapidly to 110°C. The mass spectrometer was operated in the selected ion monitoring (SIM) mode and monitored ions at m/z 156, 158, 161, and 163 with a 50 ms dwell time for each ion. Quantification was made using the ratios of the ions 163/158 and 161/156. The concentration of unlabeled bromobenzene ([BrB], in moles per mole of nitrogen) in the cylinder was calculated using the following formula:

$$\text{Amount of BrB} = RF \times \frac{\text{Response BrB}}{\text{Response IS}} \times \text{Amount IS}$$

$$[BrB] = \frac{\text{Amount of BrB}}{\text{Volume trapped}} \times \frac{\text{L nitrogen}}{\text{mole}} \times \frac{\text{moles BrB}}{\text{gram}}$$

where RF is the response factor of the labeled (perdeuterated) bromobenzene to the unlabeled and IS is the labeled bromobenzene internal standard. The volume of nitrogen, which was the make-up gas in the cylinder, was corrected for the atmospheric pressure and temperature in the laboratory on the day of analysis.

An initial attempt at quantifying an organic in a cylinder was made with a prototype version of the trap using bromobenzene in nitrogen at the 90 ppb level to test the general feasibility of the technique. One liter of

the analyte mixture was trapped and and analyzed using a GC split flow of 60:1. An IDMS value of 118 +/- 8 ppb (based on 21 measurements made over a 2 day period) was determined on this cylinder. The agreement was judged as satisfactory for an initial quantification.

The modified version of the trap as described earlier in this report was first used in January of 1984 to quantify bromobenzene in nitrogen at the 25 ppb level. The technique described above was used with a volume of 2 L trapped. The 25 ppb cylinder was analyzed on five separate days and the results are summarized in Table 2. Our result for the sample cylinder is in good agreement with the other values determined by the Gas and Particulate Sciences Division of NBS who prepared and also analyzed this cylinder. The precision obtained is limited primarily by variations in the response factors which do not involve the trap. This indicates that most of the variation lies within the GC/MS system itself.

The IDMS procedure was also used to quantify bromobenzene at the 1 ppb level. This lower concentration required trapping a larger volume of sample (4 L). The results are presented in Table 3. Two identical models of the trap were used in making these measurements and no bias was observed between the two traps. The average value of 1.51 +/- 0.14 ppb (error limits based on 2 standards deviation units) overlaps with the value of 1.33 +/- 0.1 ppb determined by the Gas and Particulate Sciences Division of NBS who prepared and also analyzed this cylinder.

Section 4. Development of a Calibration Curve Method for Quantification of Volatile Organics in Gaseous Samples

A GC/MS method based on establishing a calibration curve was developed that permits a direct comparison of the concentrations of trace components from two gas sources. This provided a means of linking data from different laboratories to a common SRM. The cryogenic trap was used for this method since it can be used with any GC system that contains a septum inlet. The principle of the calibration curve is to establish a plot of response versus amount for a particular analyte. From a measured volume of a sample with an unknown concentration of the analyte and its response, the concentration can be calculated. SRM gas cylinders, if available containing the analytes of interest, are well suited as calibrant samples because of their certified values for analytes. In order for this method to work properly, a known relationship, preferably linear, must be established over the desired concentration range. This, in turn, requires that reproducible amounts of the sample be trapped and delivered to the GC/MS for analysis.

Early experiments using the 25 ppb cylinder, a fast desorption flow (>20 mL/min), and a high split flow had shown a linear relation between volume and response from 0.5 L to 4.0 L as shown in Table 4 (counts are an arbitrary response unit). The values corrected for changes in split flow shown in the last column had a higher precision and linearity as seen by the linear correlation coefficient. Experiments were also performed using splitless injection to eliminate the need for correction from drifting split flow ratios and also to permit the calibration method to be used on systems such as those at EPA/RTP which do not have split flow capabilities. However, this greatly increases the amount of material placed on column which had the effect of reducing the useable linear range of the calibration

curve for the SRM mixtures currently available. The use of SRM cylinders of the appropiate concentration (low ppb range) as calibrants would offer a solution to this problem.

In order to demonstrate the applicability of the calibration curve method, gas samples were analyzed by the method described in the previous section. Multicomponent mixtures were used to provide a more realistic evaluation of this method. This section describes the results obtained using a four component SRM cylinder to establish a calibration curve and make measurements on two cylinders with various combinations of the analytes.

In the first set of analyses, an SRM cylinder was used that contained benzene, toluene, chlorobenzene, and bromobenzene at nominal concentrations of 250 ppb each. Minor modifications in the trapping and analysis procedure were necessary to measure the more volatile components. The desorption time was increased to 2 minutes to insure quantitative transfer of the sample under slow flow conditions (1.5 mL/min). Cryo-focusing with liquid nitrogen on the first meter of the column (see Figure 2) became necessary to produce well-defined peaks, especially for benzene and toluene. The GC was operated in the splitless injection mode and the column temperature was held at 50°C for 2.5 minutes and then taken to 100°C. The mass spectrometer was operated in the single ion monitoring mode using ions at m/z 78, 91, 112, and 156 for the analytes benzene, toluene, chlorobenzene, and bromobenzene, respectively. Figure 3 illustrates a typical ion chromatogram for the four component SRM cylinder.

Measurements were done on the SRM cylinder before and after a series of measurements on the unknown cylinders. The unknown cylinders were measured using the same GC/MS conditions. The results for one analysis are presented in Table 5. The first section of the table shows the results for the SRM cylinder and includes measurements made before and after the unknown cylinders were measured. Due to the high concentrations in the SRM cylinder and the splitless mode of injection, only two different volumes were used in the calibration curve with (0,0) included as a third point. Measurements were made at least three times for each volume. These results show all measurements to be linear with a linear correlation coefficient of > 0.999 over the volumes ranges indicated for all analytes. The units of the slope are response per unit volume which directly enters the calculation for concentration. The relative standard deviation of the slope is 5% or less for all four analytes in the SRM cylinder. The analytes in the unknown cylinders were also measured at two different volumes with duplicate measurements at each volume. A linear relationship was observed in each case. The unknown analyte concentration is calculated using the following formula:

$$\text{Sample concentration} = \text{SRM concentration} \times \frac{\text{Sample slope}}{\text{SRM slope}}$$

with concentrations for both the SRM and sample given as ppb (v/v). The measured concentrations for analyses on both cylinders are summarized in Table 6. The two earlier analyses (10/19 and 11/21 for cylinder FF9505 and 10/19 and 10/23 for cylinder FF9738) were made under conditions where the desorption flow rate was not stable and these data may reflect that insta-

bility. The latter analysis (11/26) was performed under more optimum conditions and the measured concentrations for the analytes in both cylinders was +/- 5% of the prepared values for this day.

In a second set of analyses, a gravimetric standard cylinder (CAL5723) containing the same four analytes at a slightly lower concentration (10 to 100 ppb) was used to prepare a calibration curve. The lower concentrations of analytes allowed the maximum volume trapped to be increased up to 400 mL. Cylinders FF9738 and FF9760 were used as unknowns and the results are summarized in Table 7. Good agreement was obtained in all cases with the exception of bromobenzene which was consistently measured lower than the prepared value by more than 13%. Since the unknown cylinders were at lower pressures (< 400 psi) than the calibration cylinders (> 750 psi), the bromobenzene may have been delivered in a slightly lower amount since it is the least volatile of the four analytes.

These results showed that analytes in gaseous samples could be successfully quantified using cryogenic trapping with either IDMS or through construction of a calibration curve using a standard gas cylinder. It now remained to evaluate the method at an independent laboratory. An EPA laboratory in Research Triangle Park, N. C., was selected to be this independent laboratory. The results of this evaluation are described in the next section.

Section 5. Independent Laboratory Evaluation of the System

In order to validate the procedure developed at NBS for delivering analytes from SRM cylinders to GC/MS systems using a cryogenic trap, the entire trap assembly (trap and cylinders) was transported to the Environmental Monitoring Systems Laboratory of the Environmental Protection Agency at Research Triangle Park (EPA/RTP), North Carolina. This section presents the results obtained at EPA/RTP for measurements of 2 unknown cylinders using a cylinder of known concentration as a calibrant as described above. It also presents a comparison of the amount of each analyte delivered from an SRM cylinder as calculated based on pressure, volume, and temperature measurements with the amount detected at EPA/RTP using their static dilution bottle calibrants.

The GC/MS instrument used to make the measurements at EPA/RTP was a Finnigan 4000 routinely used to analyze Tenax cartridges loaded from various types of ambient air samples. This instrument contained a 50 m glass capillary column which was held at room temperature for approximately 2 minutes (with cryo-focusing on the head of the column) then taken to 120o C at 4o per minute according to their standard operating procedure. The mass spectrometer was operated in the scanning mode from 35 to 320 amu with 0.8 seconds per scan which is also according to their standard operating conditions. This is in contrast to the system at NBS where a fused silica column was used and the mass spectrometer (Hewlett-Packard 5930) was operated in the selected ion monitoring mode when performing quantitative analyses with the cryogenic trap.

A. Determination of Unknown Cylinders using a Known Cylinder as Calibrant. The cylinders analyzed at EPA/RTP were FF9738 and FF9760 using CAL5723 as a calibrant. Measurements on these cylinders had previously been

made at NBS. A calibration curve was established for each day and multiple measurements were made on each unknown cylinder at different volumes. The results for analyses on a single day at EPA/RTP are summarized in Table 8. The point (0,0) was added to all these mesurements in calculating the slope. The linearity of the response and the reproducibility are similar to that obtained at NBS for these cylinders. The two concentrations measured at EPA/RTP for each analyte are summarized in Table 9 along with two recent results obtained at NBS. The concentrations were calculated according to the formula previously given. For all analytes in both cylinders, the average values measured at EPA/RTP are not statistically different from those determined at NBS and in good agreement with the prepared values. None of the values measured at EPA/RTP were different from the prepared values by more than 14%. The combined average value listed in Table 9 for all of the measurements made on these cylinders at both laboratories falls within 2 sigma of the prepared value for all analytes with the exception of bromobenzene in cylinder FF9760 which is slightly more than 3 sigma outside of the prepared value.

B. Comparison of Amount Delivered versus Amount Detected using a Static Dilution Bottle as Calibrant. The measurements using the cryogenic trap at EPA/RTP also afforded an opportunity to compare the amount delivered through our sytem (trap and cylinders of known concentration) with the amount measured using EPA/RTP's static dilution bottle to calibrate their Finnigan instrument. The data system on this instrument is calibrated for certain compounds, including the ones in this study, using a rigorous calibration curve generated by analyzing gaseous mixtures from static dilution bottles [1]. The data sytem is programmed to take the raw data, which is normally generated from Tenax cartridges, and produce the amount detected in nanograms. Table 10 is a listing of the measurements in chronological order and compares the nanograms delivered, based on pressure, volume, and temperature measurements, with the amount measured by the EPA/RTP instrument. The amount measured in ppb (mol/mol) is included in this table as well for comparison with the values in Tables 8 and 9. Table 11 lists the relative standard deviations for measurements made on 200 mL of cylinder CAL 5723 (the most measured sample and volume for any one day) for a series at NBS with those made at EPA/RTP. The differences in the relative standard deviations for the two sets of measurements are not significant indicating that the precision obtained at the two laboratories is similar. The amount of analyte delivered was calculated using the formula shown below which is based on the Ideal Gas Law (a good assumption for nitrogen which is the make-up gas for these samples).

$$\text{mol } N_2 = \frac{\text{Pressure (atm)} \times \text{Volume trapped (L)}}{(0.0820575\ \text{L·atm/mol·K}) \times \text{Temperature (K)}}$$

$$\text{g analyte} = \frac{\text{mol } N_2 \times [\text{mol analyte prepared}] \times \text{g analyte}}{[\ 10^9\ \text{mol } N_2\ ] \quad \text{mol analyte}}$$

The pressure and temperature used in this equation were measured in the laboratory. The average percent difference between the delivered and measured amounts for the analytes was biased in all cases with 11 to 35% more of the sample being detected than delivered. The agreement between the delivered and detected amounts were best for benzene and progressively worse for the less volatile chlorobenzene and bromobenzene as shown in Table 10.

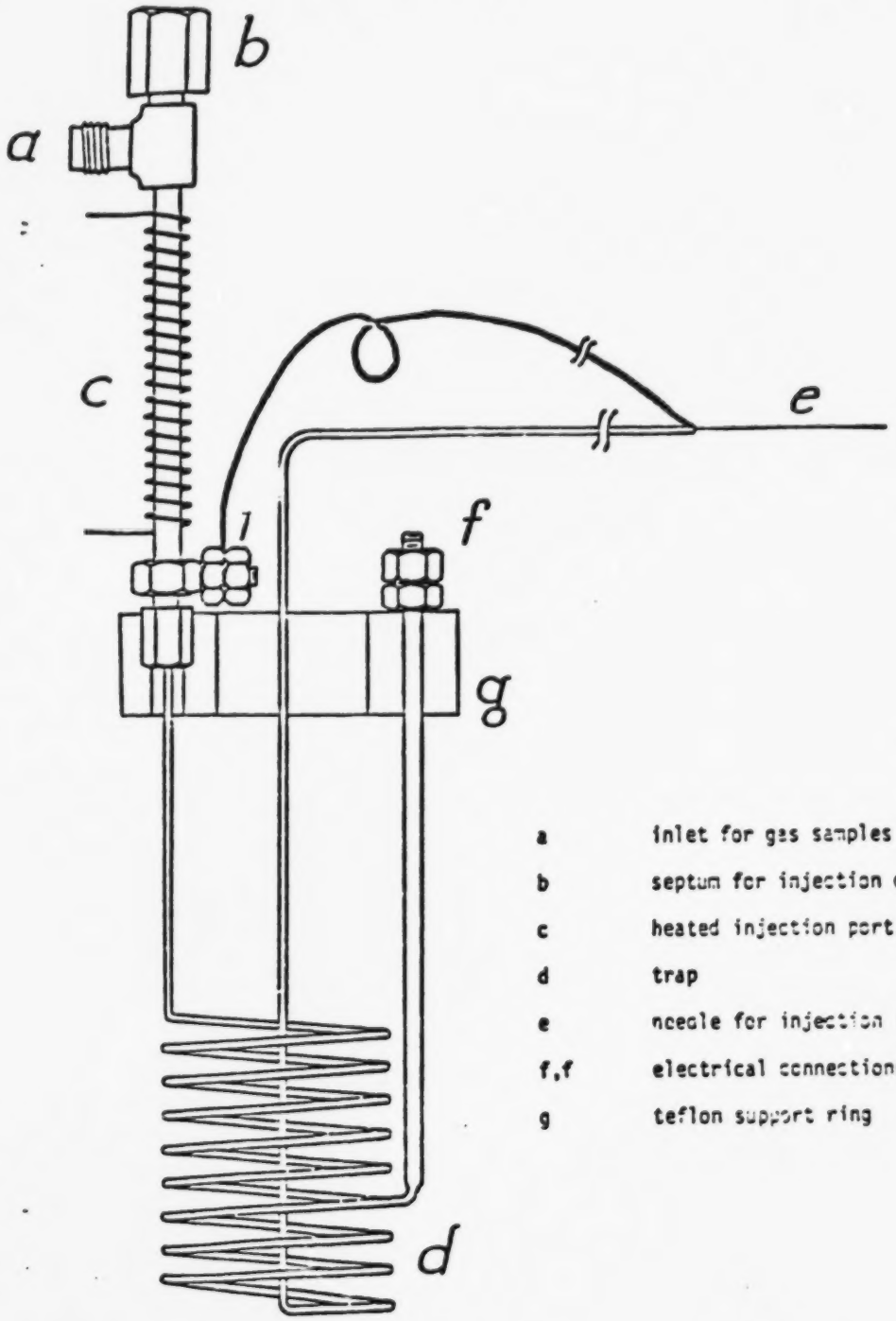
This trend indicates a systematic error between the two methods that is related to the volatility of the analyte. The discrepancy suggests that either the calibration of the data system is biased due to inefficent transfer of less volatile components from the static dilution bottles or that the cryogenic trap transfers greater amounts of the less volatile components than of the more volatile components for a given volume. One approach to this issue would be for the NBS laboratory to perform measurements on static dilution bottles used to calibrate the EPA instrument.

The agreement between the values obtained at NBS and EPA/RTP on the determination of unknown cylinders using known cylinders as calibrants demonstrated the efficacy of the trap for transferring standard gaseous mixtures to GC/MS systems. The IDMS measurements on bromobenzene samples reported previously show that the trap can provide an absolute means for determining the amount of sample delivered to a GC/MS system.

These experiments showed that the cryogenic trap can be used as a viable means of quantitatively transferring analytes in standard gaseous cylinders to GC/MS systems and can be used in conjunction with SRM cylinders to audit EPA laboratory performance.

Section 6. References

[1] Curtis Morris, Richard Berkley, and Joseph Bumgarner, Analytical Letters, 16(A20), 1585-1593 (1983).



a	inlet for gas samples or helium
b	septum for injection of liquid samples
c	heated injection port
d	trap
e	needle for injection into GC
f,f	electrical connections for heating trap
g	teflon support ring

Figure 1. Trap Used in Bromobenzene Experiments

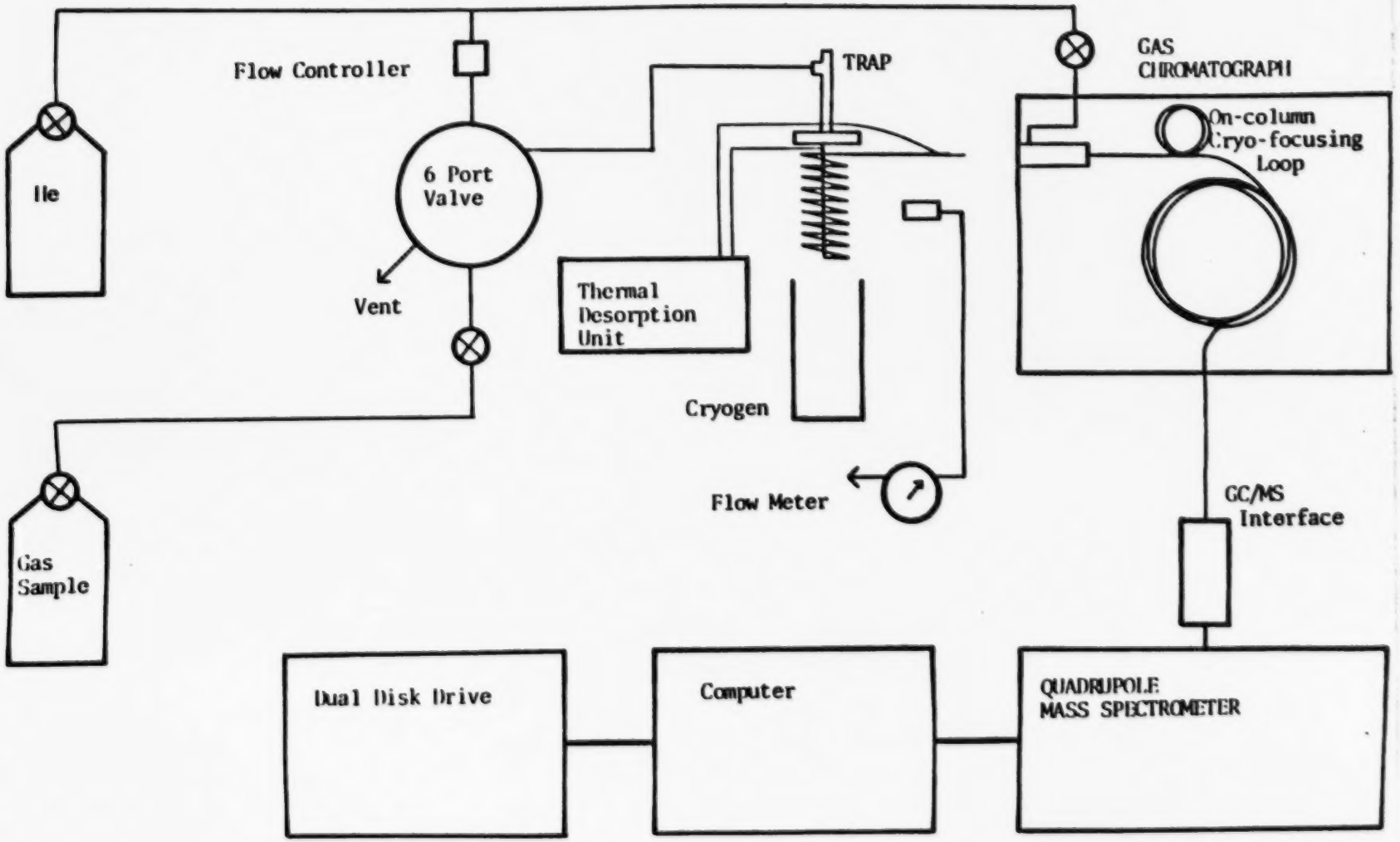


Figure 2: Diagram of system for trapping and analyzing gaseous samples.

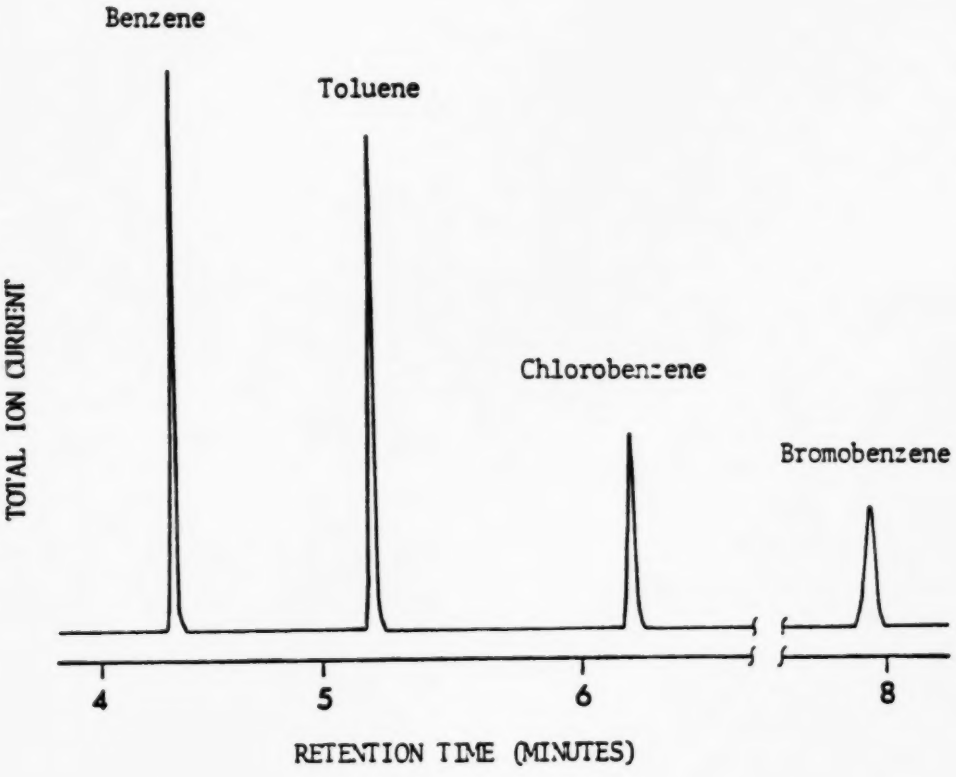


Figure 3: Total ion chromatogram of four component mixture.

Table 1

Comparison of Area Ratio Measurements of Labeled/Unlabeled Bromobenzene by Direct Injection (DI) and Trapping and Desorption (TD)

Trap Version	Method	163/158	RSD (%)	161/156	RSD (%)
Prototype	DI	0.958	1.9	0.991	1.0
	TD	0.866	20	0.886	20
Final	DI	0.898	0.3	0.912	0.7
	TD	0.897	1.7	0.902	1.4

Table 2

Determination of Bromobenzene in Cylinder CAL-5022 by GC/IDMS

Date	RF	SD_{rf}	N_{rf}	Sample	SD_s	N_s	PPB
1/13	0.9746	0.0163	4	1.2709	0.0330	2	26.63
1/17	1.0003	0.0292	9	1.2941	0.0183	2	26.91
2/10	0.9610	0.0189	4	1.2589	0.0477	2	26.51
2/21	0.9279	0.0136	7	1.3022	0.0511	4	24.74
2/22	0.9134	0.0135	5	1.2633	0.0443	5	25.11
				Average of all five:			25.98
				SD (n = 5):			0.98
				RSD (n = 5):			3.8%

RF = response factor = (cts lab/cts unl) * (ng unl/ng lab)

SD = standard deviation

N_{rf} = number of RF's measured

Sample = (cts lab/cts unl) for trapped volume + spike

N_s = number of samples measured

ppb = measured concentration of sample in ng/g

Table 3

Summary of Data from Cylinder AAL-8940: 1.33 ppb Bromobenzene in N_2

Date	RF	SD_{rf}	N_{rf}	Sample	SD_s	N_s	PPB
7/13	0.86094	0.00906	8	0.88486	0.02516	4	1.432
	0.85150	0.01218	8	0.88164	0.03079	4	1.422
7/17	0.83726	0.00921	6	0.76475	0.03804	8	1.598
	0.8396	0.00840	6	0.75890	0.04541	8	1.615
7/18	0.93822	0.00940	8	0.90048	0.05313	6	1.528
	0.94808	0.01360	8	0.91872	0.05696	6	1.514
7/19	0.94581	0.01234	8	0.88802	0.02210	5	1.542
	0.96058	0.01093	8	0.89452	0.02242	5	1.554
7/25*	0.94516	0.01134	4	0.91194	0.03173	4	1.499
	0.94982	0.01709	4	0.91853	0.02099	4	1.495
7/26*	0.91563	0.02838	6	0.90731	0.05218	5	1.459
	0.92095	0.04513	6	0.91740	0.05050	5	1.413
				Average of all six:			1.506
				SD (n = 6):			0.068
				RSD (n = 6):			4.6%

Upper set of numbers from ^{81}Br isotope; lower set from ^{79}Br isotope

RF = response factor = (cts lab/cts unl) * (ng unl/ng lab)

SD = standard deviation

N_{rf} = number of RF's measured

Sample = (cts lab/cts unl) for trapped volume + spike

N_s = number of samples measured

ppb = measured concentration of sample in ng/g

*Different trapping apparatus used

Table 4

Response in Counts of Bromobenzene as a Function of Volume Trapped

Volume Trapped	Counts[1]	Counts per Liter	Split Flow	Counts per Liter[2]
4 L	126720	31680	98	31680
2 L	62293	31146	96	30510
1 L	33363	33363	90	30639
0.5 L	17997	35994	86	31586
Average of all four:		33046		31104
SD (n = 4):		2181		615
RSD (n = 4):		7%		2%

Linear correlation (volume versus normalized counts) = 0.99973

[1]Average counts for m/z 156 and 158

[2]Normalized to a split flow of 98 mL/minute

Table 5

Data for Calibration Plot and Analysis for a Single Day

Cylinder	Volume in mL		Analytes BEN	TOL	CLB	BRB
114-5A	100	$x_{n=3}$ =	30126	35651	19909	19451
		RSD =	11%	5%	6%	14%
	200	$x_{n=4}$ =	64861	72492	41737	37908
		RSD =	7%	4%	9%	11%
		CORR =	0.99915	0.99996	0.99965	0.99988
		SLOPE =	324 ± 16	362 ± 4	209 ± 7	190 ± 4
FF 9505	200	$x_{n=2}$ =		29719	17041	
		RSD =		2%	3%	
	400	$x_{n=2}$ =		62552	34814	
		RSD =		3%	<1%	
		CORR =		0.99959	0.99993	
		SLOPE =		156 ± 6	87.0 ± 1.3	
		CONC =		96.5	91.6	
FF 9738	150	$x_{n=2}$ =	7290		7317	22122
		RSD =	6%		<1%	3%
	300	$x_{n=2}$ =	16072		15974	40238
		RSD =	6%		8%	15%
		CORR =	0.99857		0.99883	0.99912
		SLOPE =	53.6 ± 3.5		53.2 ± 3.2	137 ± 7
		CONC =	39.2		56.0	157

x = average response in counts
RSD = relative standard deviation
CORR = linear correlation of volume trapped to response
SLOPE = counts per mL volume trapped
CONC = calculated concentration in ppb

Table 6

Comparison of Measured[1] and Prepared[2] Concentrations in ppb for Two Cylinders Using Cylinder 114-5A as Calibrant

Cylinder	Date	BEN	TOL	CLB	BRB
FF 9505	10/23		84.8	83.6	
	11/21		102	92.0	
	11/26		96.5	91.6	
	Average		94.4	89.1	
	RSD		9%	5%	
	Prepared		101	96	
FF 9738	10/19	37.9		38.2	142
	10/23	36.5		48.1	130
	11/26	39.2		56.0	157
	Average	37.9		47.4	143
	RSD	4%		19%	10%
	Prepared	39.1		53.2	160

[1]Measured using cryogenic trap and standard cylinder as calibrant in the Organic Analytical Research Division.

[2]Prepared in the Gas and Particulate Science Division.

Table 7

Comparison of Measured[1] and Prepared[2] Concentrations in ppb for Two Cylinders Using Cylinder CAL 5723 as Calibrant

		Analytes			
Cylinder		BEN	TOL	CLB	BRB
FF 9738	measured	35.8	---	50.4	128
	prepared	39.1	---	53.2	160
FF 9760	measured	23.8	---	11.2	16.0
	prepared	22.9	---	11.3	18.4

[1]Measured using cryogenic trap and standard cylinder as calibrant in the Organic Analytical Research Division.

[2]Prepared in the Gas and Particulate Science Division.

Table 8

Data for a Calibration Plot and Analysis of Two Cylinders
During a Single Day (January 25, 1985) at EPA/RTP

Cylinder	Volume (in mL)		Benzene	Chlorobenzene	Bromobenzene
CAL 5723	200	$x_{n=2}$ =	121168	13327	142840
		RSD =	7%	5%	4%
	400	$x_{n=2}$ =	225600	26616	277660
		RSD =	2%	2%	3%
		INTER =	2789	6	1337
		SLOPE =	564 ± 35	694 ± 26	419 ± 13
		PREP =	101.8	93.2	50.4
FF 9738	100	$x_{n=2}$ =	22788	39832	150618
		RSD =	18%	21%	23%
	200	$x_{n=1}$ =	45245	79901	288850
		RSD =	---	---	---
	300	$x_{n=1}$ =	71338	123008	428060
		RSD =	---	---	---
		INTER =	-628	-679	3520
		SLOPE =	236 ± 25	409 ± 49	1422 ± 201
		CONC =	42.6	54.9	171
		PREP =	39.1	53.2	160
FF 9760	600	$x_{n=2}$ =	80129	44410	87833
		RSD =	2%	1%	2%
	1200	$x_{n=2}$ =	138256	86426	168914
		RSD =	3%	12%	12%
		INTER =	3667	732	1125
		SLOPE =	115 ± 11	72.0 ± 5.2	141 ± 10
		PREP=	22.9	11.3	18.4

x = average response in counts
RSD = relative standard deviation
INTER = intercept
SLOPE = counts per mL volume trapped
PREP = prepared concentration in ppb (mol/mol)
CONC = calculated concentration in ppb (mol/mol)

Table 9

Comparison of Values Measured at NBS and EPA/RTP Versus Calibrant Cylinder with Prepared* Concentrations (ppb) for Cylinders FF 9738 and FF 9760

Cylinder	Laboratory	Benzene	Chlorobenzene	Bromobenzene
FF 9738	NBS	39.2, 35.8	56.0, 50.4	157, 128
	EPA/RTP	41.9, 42.6	52.1, 54.9	160, 171
	Combined	39.9 ± 3.1	53.4 ± 2.6	154 ± 18
	n = 4			
Prepared Concentration		39.1	53.2	160
FF9760	NBS	23.8, 26.1	11.2, 7.7	16.0, 17.2
	EPA/RTP	23.9, 20.8	12.2, 9.7	16.6, 17.0
	Combined	23.6 ± 2.2	10.2 ± 2.0	16.7 ± 0.5
	n = 4			
Prepared Concentration		22.9	11.3	18.4

*Prepared gravimetrically by the Gas and Particulate Science Division of NBS.

Table 10

Comparison of the Calculated Amount Delivered by the Trap (DELIV)
Versus the Amount Detected by the EPA/RTP Instrument* (MEAS)

		Benzene					Chlorobenzene					Bromobenzene				
FILE	CYLINDER	DELIV (NG)	MEAS (NG)	DIFF (NG)	PERCENT DIFF	MEAS (PPB)	DELIV (NG)	MEAS (NG)	DIFF (NG)	PERCENT DIFF	MEAS (PPB)	DELIV (NG)	MEAS (NG)	DIFF (NG)	PERCENT DIFF	MEAS (PPB)
114	CAL 5723	65	78	13	20	122	86	118	32	37	128	65	110	45	69	85
115		65	82	17	26	128	86	120	34	40	130	65	107	42	65	83
116		130	156	26	20	122	172	231	59	34	125	130	196	66	51	76
117	FF 9760	29	35	6	21	28	21	29	8	38	15	47	63	16	34	25
118		59	68	9	15	26	41	53	12	29	14	95	124	29	31	24
119		88	90	2	2	23	62	77	15	24	14	142	182	40	28	24
120		88	97	9	10	25	62	74	12	19	13	142	177	35	25	23
121	CAL 5723	65	66	1	2	104	86	102	16	19	111	65	90	25	38	70
122		130	121	-9	-7	95	172	198	26	15	107	130	167	37	28	64
123	FF 9738	25	30	5	20	47	49	67	18	37	73	206	286	80	39	222
124		50	51	1	2	40	98	109	11	11	59	412	483	71	17	187
125		12	14	2	17	46	25	34	9	36	72	103	151	48	47	235
126		12	16	4	33	52	25	37	12	48	78	103	169	66	64	262
127		25	29	4	16	45	49	65	16	33	71	206	285	79	38	221
129	CAL 5723	65	64	-1	-2	100	85	92	7	8	101	64	75	11	17	59
130		65	67	2	3	105	85	101	16	19	111	64	85	21	33	67
131		130	132	2	2	104	171	192	21	12	104	129	160	31	24	62
132	FF 9738	12	17	5	42	56	24	39	15	63	88	102	168	168	66	264
133		25	28	3	12	44	49	62	13	27	68	205	271	66	32	211
134		37	43	6	16	45	73	91	18	25	66	307	402	95	31	210
135		12	14	2	17	46	24	30	6	25	66	102	125	23	23	197
136	CAL 5723	65	74	9	14	116	85	107	22	26	117	64	89	25	39	70
137		130	131	1	1	103	171	198	27	16	108	129	167	38	29	65
138	FF 9760	44	49	5	11	25	31	39	8	26	14	71	88	17	24	23
139		87	79	-8	-9	21	62	72	10	16	13	141	175	34	24	23
140		87	81	-6	-7	21	62	62	0	0	11	141	149	8	6	20
141		44	47	3	7	24	31	38	7	23	14	71	89	18	25	23
		AVE PERCENT DIFF			11 ± 12		AVE PERCENT DIFF			26 ± 13		AVE PERCENT DIFF			35 ± 16	

*Calibrated with static dilution flasks

PERCENT DIFF = (MEAS - DELIV)·100/DELIV

PPB = parts per billion, mole/mole calculated as:
(ng detected/L trapped)·(mol analyte/ng)/(mol N /L)

Table 11

Comparison of the Relative Standard Deviations (RSD) for Measurements Made on Cylinder CAL 5723 at EPA/RTP with Those Made on December 27, 1984, at NBS.*

Volume	Analyte	NBS RSD (n=5)	EPA/RTP RSD (n=6)
200 mL	Benzene	14%	10%
	Toluene	14%	17%
	Chlorobenzene	15%	10%
	Bromobenzene	11%	14%

*The EPA/RTP RSD is based on the amount detected by their data system per volume trapped and the NBS RSD is based on the total number of counts per volume trapped.